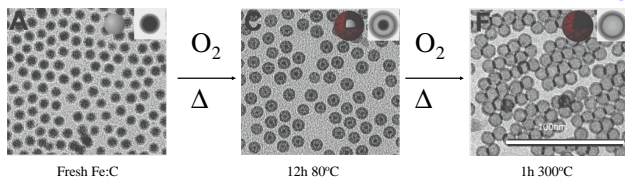


# Oxidation kinetics of Fe-C nanoparticles in the Kirkendall-hollowing regime

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## Intro: Oxidation of metal nanospheres results in their becoming hollow via Kirkendall effect



This phenomenon has potential uses for catalysis and other kinds of nano-chem. Further, nano-Fe oxides are important materials in nature and have uses in recording media, in-vivo MRI, water treatment etc.

To understand the kinetics, we need to know:

1: What is the starting material? 2: What does it become? 3: What are the kinetics vs. time and temperature?

### Experiments

**Synthesis:** Fe(CO)<sub>5</sub> was added to air-free octadecene or squalane, with oleylamine or oleic acid as a surfactant at 200C and stirred for 20min, resulting in a black suspension of magnetic nanoparticles. EXAFS shows them to be amorphous Fe:C alloy. Particle size could be tuned from 8-10nm by changing reaction conditions.

**Reaction:** For the SAXS experiment, particles made in squalane were reacted with dry air in a mica-windowed in-situ cell while SAXS patterns were being taken for times up to 2 hours at temperatures up to 150C. Ar purge and anaerobic transfer were used to keep the reaction from happening until the start of measurement. Buffer measurement was done by refilling the cell with pure squalane at the same temperature as the reaction. The average unoxidized particle size was about 8nm, as determined by SAXS.

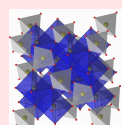
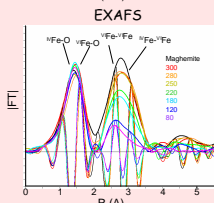
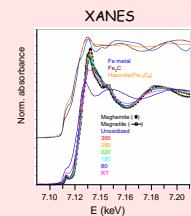
For EXAFS measurements, a batch of particles were made in octadecene/octylamine and divided into 6 parts. Each of these parts was oxidized in solution at a different temperature: RT, 80, 120, 180, 220 or 250 C. The oxidation was carried out by flowing 20% O<sub>2</sub> in Ar through the solution in a 3-neck flask for ~2 hours. Part of the 250C batch was re-oxidized at 280C and another part at 300C. Measurements were done at RT. Laboratory SAXS yielded an average diameter of 10 nm for the unreacted particles in this batch.

**Measurement:** SAXS measurements were done at the DUBBLE beamline at ESRF using a 1.4m path length at 12keV;  $q$ -range 0.33-3nm<sup>-1</sup>. Data fitting was done with a shell-model using home-built LabVIEW software.

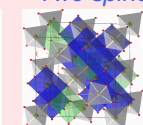
XAS measurements were done on capillary samples at ALS 10.3.2 at the Fe K-edge. A large database of Fe standards was used for comparison. The beamline suite of software plus Artemis was used for data reduction and analysis.

### XAS: Isochronal oxidation

Measure XAS as a function of oxidation temperature at time=2hr



Magnetite



Maghemite

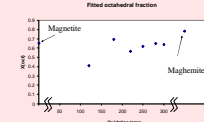
The unoxidized particles show very weak EXAFS and no diffraction, suggesting an amorphous alloy. C is a plausible alloy element, the only one. At low temps, the XANES multicomponent fits show the presence of Fe carbides. Note shift of main edge rise indicating valence change towards Fe<sup>3+</sup> as well as metal/carbide-like pre-edge step.

At all temps above RT, the same basic structures appear, which are shared by magnetite and maghemite (see below).

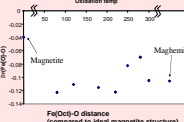
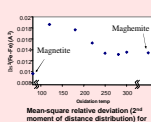
Octahedral and tetrahedral Fe exist, with octahedra edge-sharing with octahedra and corner-sharing with tetrahedra. What changes is the disorder in the Fe-Fe distances, which is quite high for the low-T oxides.

### Two spinel Fe oxides:

Maghemite is magnetite (Fe-Fe spinel) with enough Fe vacancies (partially-occupied sites shown in green) to balance a Fe<sub>2</sub>O<sub>3</sub> stoichiometry.



Structural parameters of nanos evolve toward those fitted for maghemite with rising temperature. Sintering at high T yields crystalline maghemite.

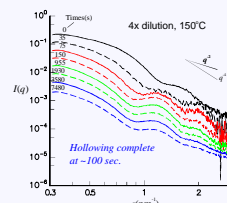
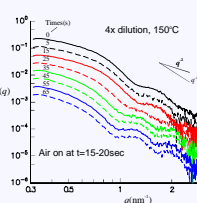


### SAXS: Isothermal kinetics

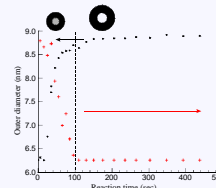
Measure small-angle scattering (at ESRF) to see size and hollowing as functions of time and temperature.

Example: 150°C oxidation.

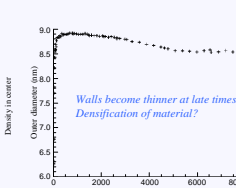
Successive curves are offset vertically for display



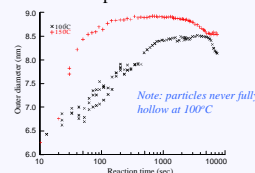
### Early-stage kinetics



### Later-stage kinetics



### Comparison of kinetics at two temperatures



The differences in the shape of the diameter vs. time curve and in final diameter may be related to temperature dependence of the final oxide's structure.

This type of work can now be performed on ALS beamline 7.3.3

### Conclusions

1. Oxidation of metal nanoparticles is a complex process, yielding a mixture of carbides and oxides at low temp, and disordered maghemite-like (off-stoichiometric spinel) oxide at higher temps, converging towards maghemite at the highest temperature.

2. The kinetics of hollowing don't follow a simple scaling law with temperature, possibly because of the complex reaction scheme above. The kinetics also seem to depend on nanoparticle concentration.

3. Simple models of reacting nano-materials are inadequate to describe the real system. Even simple materials can become complex.

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